Applied Catalysis B: Environmental 84 (2008) 691–698

Contents lists available at ScienceDirect

Applied Catalysis B: Environmental

journal homepage: www.elsevier.com/locate/apcatb

Photocatalytic activity of TiO_2-based materials for the oxidation of propene and benzene at low concentration in presence of humidity

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ARTICLE INFO

Article history:
Received 13 February 2008
Received in revised form 29 May 2008
Accepted 3 June 2008
Available online 11 June 2008

Keywords:
Photocatalysis
TiO_2
Oxidation
Propene
Benzene

ABSTRACT

This paper complements previous studies devoted to the photocatalytic oxidation of a low-concentration propene gaseous stream in absence of humidity using agglomerated TiO_2-based materials. These prepared agglomerated materials have shown very good oxidation activities and complete selectivity towards CO_2. The present paper analyses the role of humidity on propene oxidation, which has not been studied before, and extends the use of the prepared agglomerated photocatalysts to low concentration benzene oxidation, both in absence and presence of humidity. The obtained results have shown that humidity must be totally avoided, or kept as low as possible, to achieve high propene conversions. In the case of benzene, some insight to controversial published results is given; very low conversions together with benzene cracking on the surface of the photocatalyst occur in absence of humidity. However, the introduction of humidity leads to high conversions and avoids benzene cracking. The performance of the agglomerated photocatalyst containing a high surface area activated carbon (TiO_2/C1) must be underlined in terms of activity.

1. Introduction

Volatile organic compounds (VOCs) are pollutants usually found in the atmosphere of all urban and industrial areas [1,2]. Propene appears in vehicle emissions and in many industrial applications such as petrochemical plants, foundry operations and others [3,4]. Moreover, it is one of the sources of indoor air pollution since it is one of the principal components of tobacco smoke [3,5]. Benzene is found in petroleum hydrocarbons and in other common environmental contaminants [6]. Most VOCs, such as propene and especially benzene, are toxic and carcinogenic to human health [6].

Among the technologies developed for the treatment of low-concentration VOC gaseous streams, heterogeneous photocatalytic oxidation (PCO) is considered to be a promising technology to decompose various organic compounds at ambient temperature to final non-toxic products such as H_2O and CO_2 [2,7]. Titanium dioxide (TiO_2) is usually the preferred photocatalyst because it is considered to be relatively inexpensive, chemically stable and has been extensively studied in ultraviolet (UV) induced photocatalytic reactions [8].

PCO of propene at low concentration has been scarcely studied in the literature [9–11]. Contrarily, several papers have been devoted to the PCO of benzene [2,7,8,12–26], as well as to the PCO of other volatile organic compounds such as toluene [1,16,24,27,28], formaldehyde [28–30] and others [16,28].

The papers dealing with the oxidation of propene have shown good results [9–11]. However, this is not the case for benzene. TiO_2 shows a poor activity and a yellowish compound is formed on the surface of the photocatalyst [16,17,22,23]. Some authors explain the yellow colour as a consequence of the formation of polymeric species [31], or relate it with compounds such as phenol, hydroquinone, 1,4-benzoquinone and other organic compounds [17,22,23].

Some works have investigated a large number of variables that may influence VOC degradation. These variables include concentration of oxygen [14,19] and VOCs [2,12–14,23], humidity [2,12,13,15,19,23], light intensity [2,8], type, amount and conformation of the photocatalyst [7,15,18,24], temperature [12,13,19] and even the reactor configuration [12]. Photocatalytic technology should be applied to the wide humidity range encountered in real gaseous streams or indoors environments [32]. However, the effect of humidity in the photocatalytic reactions in gaseous phase still remains unclear.

In the case of PCO of propene, no studies dealing with the effect of the presence of water vapour can be found in the literature, which is not the case for the PCO of benzene. Thus, as an example,

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doi:10.1016/j.apcatb.2008.06.002

Wang et al. [2] study different relative humidity percentages ranging from 0.5% to 80% and indicate that the removal of benzene rapidly increases with the relative humidity (R.H.) in the range of 0.1–10%, but then the conversion decreases for humidity percentages larger than 10%. d'Hennezel et al. [17] demonstrated that the presence of water vapour is necessary for a continuous benzene conversion. These authors reported high initial benzene conversions followed by a decrease over time using three different relative humidity percentages (0%, 4% and 34%) [17]. Finally, the conversion after 3 h of reaction was stabilized at some determined value [17].

Doucet et al. [23] showed that the increase in relative humidity led to a decrease in the conversion at short times and an increase in the conversion at long times. In contrast, Fu et al. [19] claimed that conversion of benzene was not affected by adding water vapour to the benzene stream.

From these results, some authors consider that water vapour plays an important role in the formation of hydroxyl radicals ($OH^{\bullet}$) on the surface of photocatalyst, that take part in the photocatalytic reaction [2,23,27,33]. Nevertheless, even in absence of water (0% of humidity), some papers have shown that benzene can be oxidised because traces of water are present on the surface of TiO_2 [17,23]. Additionally to these results, others have concluded that the presence of an excessive amount of water vapour inhibits the photocatalytic activity; probably as a result of the competition between water vapour and the organic compounds to be adsorbed on the active sites [12,27].

To clarify the effect of the presence of water on the photocatalytic oxidation of propene and benzene, the present paper deals with four different photocatalysts: (i) TiO_2 in form of powder (P25 from Degussa), (ii) TiO_2-pellets containing 100% TiO_2 (prepared from TiO_2 P25 from Degussa), (iii) TiO_2-based pellets containing activated carbon and (iv) TiO_2-based pellets containing MCM-41. Agglomerated titania would be the preferred form in gaseous applications [33–35].

The selection of these three TiO_2-based photocatalyst pellets, previously used for the PCO of propene in absence of humidity [10,11], will allow us to complement our previous results and to confirm some activity improvement when incorporating carbon or inorganic materials on the TiO_2-based pellets.

Hence, the present study focuses on the photocatalytic oxidation of either propene or benzene by four different TiO_2-based photocatalysts analysing the importance of humidity on the obtained results.

2. Experimental

2.1. Photocatalysts preparation and characterisation

As explained in the introduction section, the performance of four different photocatalysts is compared. One is commercial TiO_2 P25 from Degussa (P25). The three other photocatalysts were prepared in form of pellets by using P25 as precursor. P25-pellets were prepared from P25 and agglomerated in the experimental conditions detailed elsewhere [10,11]. The other two photocatalysts were prepared using P25 and an additive, either MCM-41 or an activated carbon. Table 1 summarises some features of these materials. The composition of the photocatalyst pellets containing an additive is 70 wt.% P25 and 30 wt.% additive and the preparation conditions for these photocatalysts are the same as those for P25-pellets and can be found elsewhere [10,11]. Table 2 compiles the nomenclature, origin, composition and shape of the four photocatalysts.

Porous texture characterisation of P25 and the additives used in the preparation of the photocatalyst pellets was performed by physical adsorption of gases, nitrogen and carbon dioxide adsorption at −196 and 0 °C, respectively, using an Autosorb-6B apparatus from Quantachrome. The BET specific surface area and the total micropore volume (DR N_2) were assessed by N_2 adsorption at −196 °C and the narrow micropore volume (DR CO_2) was determined by CO_2 adsorption at 0 °C [37]. Table 1 compiles the porous texture characterisation.

Table 1
Porous texture characterisation of the materials used in the preparation of the TiO_2-based materials

Sample	Type of material	BET surface area (m^2/g)	DR N_2 (cm^3/g)	DR CO_2 (cm^3/g)
P25	TiO_2	54	0.02	0.02
M1	MCM-41	1092	0.44	0.20
C1	AC[a]	3091	1.10	0.66

[a]Activated carbon prepared by KOH activation using the experimental conditions detailed elsewhere [36].

2.2. Experimental conditions for PCO of benzene or propene at low concentration

The experimental system used in benzene and propene PCO tests was designed in our laboratory. It consists of a quartz reactor (cut-off <200 nm) where the photocatalyst bed is placed on quartz wool. The reactor is 50 mm height, its diameter is 20 mm and the quartz wool support height is around 10 mm. An 8 W Philips UV lamp is placed parallel to the quartz reactor, in a distance around 1 cm. The UV lamp radiation peak appears at 257.7 nm (UV-C). The commercial reference of the lamp is TUV 8 W FAM. The couple quartz reactor–lamp is surrounded by a cylinder covered by tinfoil. A scheme of this system is detailed elsewhere [10].

The weight of catalyst was selected so as to have constant weight of TiO_2. Thus, 0.11 g of P25 (powder) are used, whereas for photocatalyst pellets (P25-pellets, TiO_2/M1 or TiO_2/C1) 0.16 g are used. For this amount of sample the typical photocatalyst bed height is around 1 mm.

The photocatalysts were used for the oxidation of benzene or propene at 100 ppmv in air at room temperature. The calibrated gas cylinders were supplied by Carburos Metálicos, S.A. Different flow rates of the VOC stream, from 7.5 to 60 ml/min (STP), were tested. These flow rates were controlled by automated mass flow-controllers (Brook Instruments).

Some oxidation experiments were performed with these gases in absence of humidity. However, the effect of humidity was also analysed. In order to introduce variable amounts of humidity in the benzene or propene flow streams, the gases passed through a bubbler containing distilled water whose temperature was controlled by using a cooling bath. Major attention was paid to the effect of bubbling the VOC gaseous stream through water at temperatures close to room temperature. Thus, in most experiments, water temperature was kept constant at 22 °C by using a cooling bath (Thermo Scientific NESLAB RTE-740 Digital Plus Refrigerated Bath). The relative humidity percentage in the stream was measured using a portable universal meter (MA2390-5S) coupled to a temperature and humidity probe (FHA646R) from Ahlborn. In these experimental conditions (water temperature 22 °C and room temperature 23 °C) the relative humidity

Table 2
Nomenclature, origin, composition and shape of the TiO_2-based materials, where

Sample	Origin	Composition (%)	Shape
P25	Commercial	100% TiO_2	Powder
P25-pellets	Prepared	100% TiO_2	Pellets
TiO_2/M1	Prepared	70% TiO_2/30% M1	Pellets
TiO_2/C1	Prepared	70% TiO_2/30% C1	Pellets

percentage in the gaseous stream was measured as 93%. Other water temperatures were selected to get lower relative humidity percentages. In the case of propene, water temperatures selected were −9, 7 and 22 °C, leading to relative humidity percentages of 12%, 38% and 93%, respectively. For benzene-gaseous streams, studied temperatures did not include temperatures lower than 7 °C since benzene freezing point is 5.5 °C [38]. Hence, with the experimental set-up used in the present study, for benzene experiments the water temperatures chosen were 7, 10 and 22 °C, leading to relative humidity percentages of 38%, 46% and 93%, respectively.

The VOC stream, either with or without humidity, passed through the photocatalyst bed and, afterwards, to a mass spectrometer (Balzers, Thermostar GSD 301 01). After suitable calibrations, the mass spectrometer permits to follow the evolution of the concentration of benzene or propene in the outlet gas with time. The experiments were repeated at least two times for checking reproducibility. VOC conversion was calculated using the following expression:

$$\text{VOC conversion}\,(\%) = \frac{C_{\text{VOC initial}} - C_{\text{VOC stationary}}}{C_{\text{VOC stationary}}} \times 100$$

where $C_{\text{VOC initial}}$ is the initial VOC concentration, 100 ppmv, and $C_{\text{VOC stationary}}$ is the stationary VOC concentration in the photocatalyst bed outlet gas when the UV is switched-on. In all cases, the VOC conversion percentages in repeated experiments differ less than 3%.

The amount of carbon dioxide after the oxidation was quantified by mass spectrometry, using a calibrated CO_2-cylinder with a concentration of 300 ppmv.

The UV-C irradiance of the lamp has been measured at 0.5 cm of the UV lamp in order to provide an order of magnitude indication of such radiation. For that purpose, a portable Delta Ohm radiometer (model HD 2102.2) with a UV-C probe (LP 471 UVC) was used (maximal measuring wavelength: 260 nm; peak width: 220–280 nm). In the measuring conditions, the accuracy is 98%. In such conditions, the UV-C irradiance is 5.7 mW/cm^2.

Temperature in the photocatalyst bed while the oxidation is taking place has also been measured using the portable universal meter (MA2390-5S) coupled to the temperature and humidity probe (FHA646R) from Ahlborn.

3. Results and discussion

In the following, the results regarding the characterisation of the photocatalysts from the point of view of porosity and activity are presented and discussed in detail.

3.1. Photocatalysts

Fig. 1 compiles the nitrogen adsorption isotherms of the materials used for the preparation of the photocatalysts. Fig. 1A, which corresponds to TiO_2 P25, shows a type II isotherm, indicative of a non-porous or macroporous material [39]. Fig. 1B presents the isotherms of M1 and C1. The isotherm of M1 (MCM-41) is type IV, which corresponds to a material with an important mesoporous contribution. The isotherm of C1 (an activated carbon) is type I corresponding to a microporous adsorbent. The porous texture characterisation of all these materials is compiled in Table 1. Table 1 shows that the specific surface area of the TiO_2 precursor (P25) is in the range of 50 m^2/g, as already reported [39]. Porosity and porosity distribution of the two additives used in the preparation of the photocatalysts is variable. BET surface area in sample M1 is in the range of 1000 m^2/g, whereas it gets to values higher than 3000 m^2/g for C1.

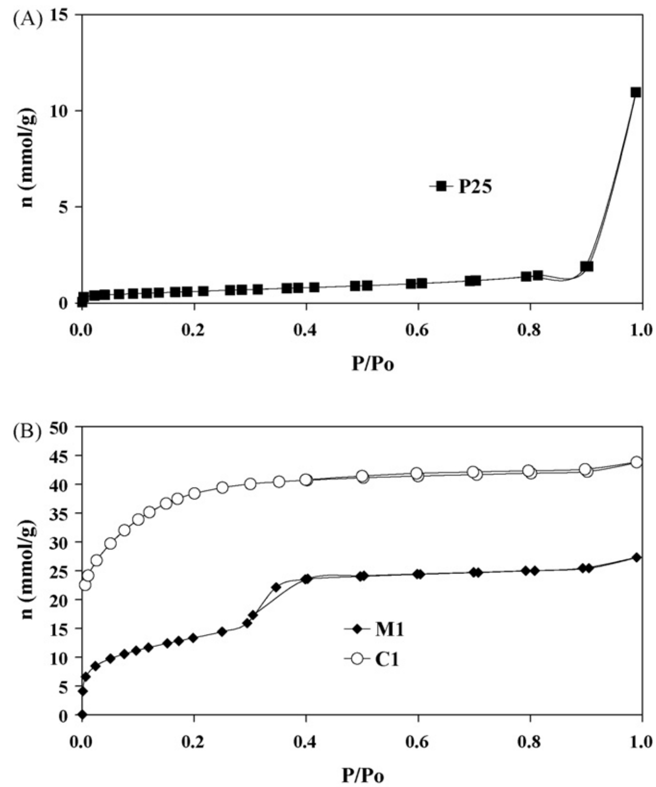

Fig. 1. Nitrogen adsorption isotherms at −196 °C of (A) P25 and (B) the additives used in the preparation of some TiO_2-based materials.

Table 2 compiles the nomenclature, origin, composition and shape of the four photocatalysts used in the present study. They include P25, a commercial photocatalyst in form of powder (used as a reference in most studies) and three photocatalysts agglomerated in form of pellets prepared in our lab. P25-pellets are 100% TiO_2, whereas TiO_2/M1 and TiO_2/C1 were prepared by a mixture of TiO_2 and an adsorbent, either MCM-41 or an activated carbon [36]. As previously reported, the preparation of agglomerated photocatalysts was performed so that they could be used in gas applications [10]. The introduction of adsorbents, either carbon or inorganic materials, in the composition of the photocatalyst was done with the aim of recovering some of the activity of TiO_2 lost after the agglomeration [10], and taking into account the advantages of the incorporation of adsorbents, such as the concentration by adsorption of the organic compounds on the adsorbents or the improvement in oxidation kinetics [40–43].

These photocatalysts have been successfully used before in the oxidation of propene in absence of humidity [10,11].

3.2. Activity of the photocatalysts

3.2.1. Propene oxidation

The presence of water has not been studied on the photocatalytic oxidation of propene at low concentration. Considering its presence in most real streams, the present paper analyses its role on the PCO of propene. Fig. 2 compares, as an example, the performance of P25-pellets towards the oxidation of propene at a flow rate of 7.5 ml/min in absence (Fig. 2A) and presence of humidity (Fig. 2B, using 93% R.H.). Comparison of both figures clearly shows that the introduction of water in the stream to be oxidised is detrimental both from the point of view of propene conversion and its kinetics. Thus, after the UV-light is switched-on, the stationary propene concentration in absence of humidity is in

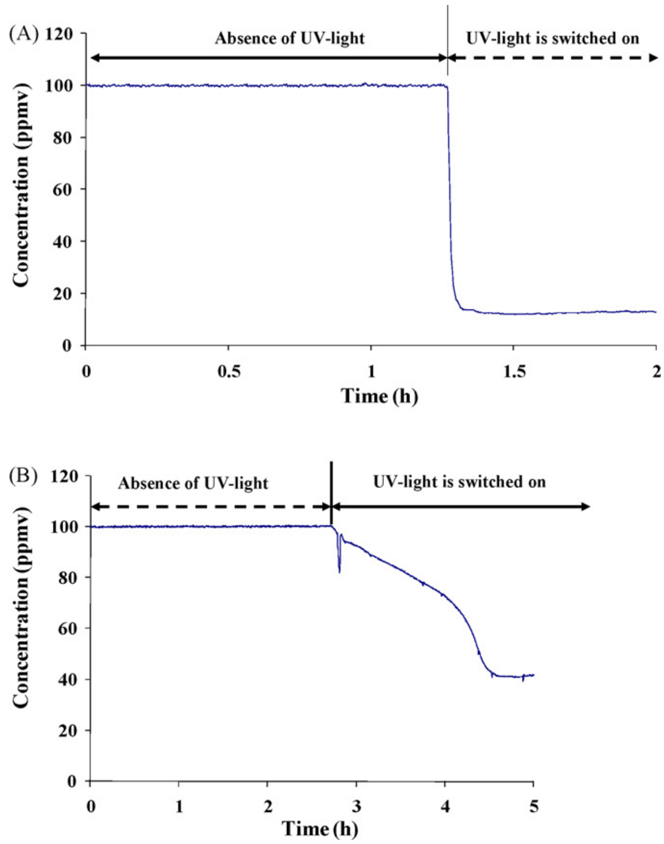

Fig. 2. Propene photocatalytic oxidation by P25-pellets in (A) absence of humidity and (B) presence of 93% R.H. (propene flow rate 7.5 ml/min in both cases).

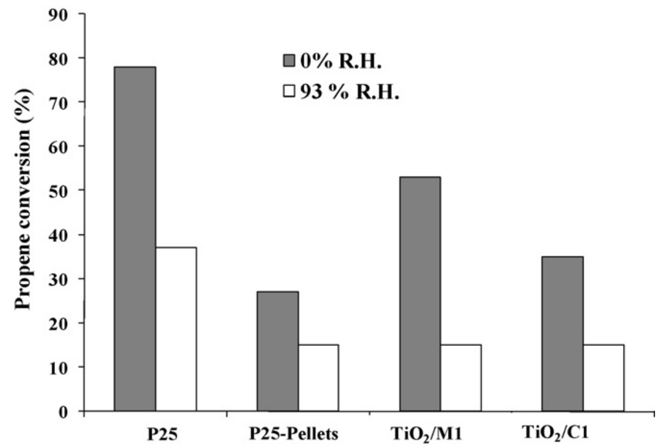

Fig. 3. Effect of the humidity on the oxidation of propene by four different TiO_2-based photocatalysts (propene flow rate 30 ml/min).

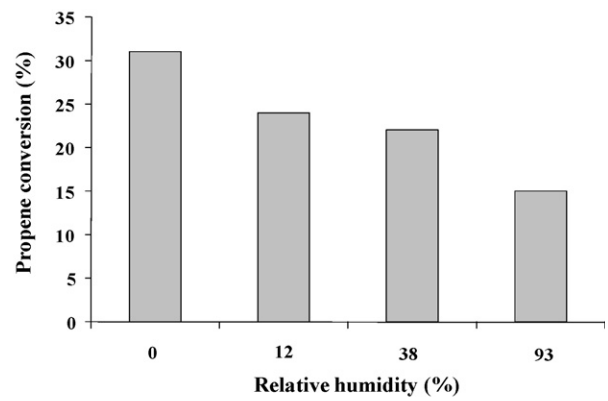

Fig. 4. Effect of different relative humidity percentages on the oxidation of propene by P25-pellets (propene-stream flow rate 30 ml/min).

the range of 13 ppmv (Fig. 2A), whereas in presence of humidity it is 43 ppmv (Fig. 2B). Also, Fig. 2A shows that the decrease in the propene concentration after the UV-light is switched-on is instantaneous, whereas this decrease is slow in presence of humidity. A similar behaviour is observed for all the samples studied and for the different flow rates tested. Table 3, which compiles propene conversions for the experimental conditions tested calculated using the formula previously presented, clearly indicates the detrimental effect of water in the stream and the importance of avoiding its presence.

To summarise these results, Fig. 3 compares, for a given flow rate (30 ml/min), the performance of the four photocatalysts in propene oxidation in absence and presence of humidity. For these experimental conditions propene conversion in presence of 93% R.H. is much lower than that achieved in absence of humidity.

The same behaviour is observed for the four catalysts in all the experimental propene flow rates studied: the conversions are much lower and the oxidation kinetics is slower in presence of 93% relative humidity, confirming its detrimental effect.

In order to understand the importance of the relative humidity percentage on propene oxidation, experiments were performed at 30 ml/min flow rate in absence of humidity and using different humidity percentages. Such information is summarised, as an example, for sample P25-pellets in Fig. 4. This figure shows that, whatever the humidity percentage, the presence of humidity is always detrimental, its negative effect being more important for higher relative humidity percentages.

The oxidation products of propene have been followed and quantified in presence and absence of humidity. In both cases total oxidation of this hydrocarbon to carbon dioxide and water takes

Table 3
Propene conversion using the four selected photocatalysts in presence or absence of humidity at different gas flow rates

Sample	Relative humidity (%)	Conversion at 7.5 ml/min	Conversion at 30 ml/min	Conversion at 60 ml/min
P25	0	100	78	50
P25	93	74	37	11
P25-pellets	0	87	31	16
P25-pellets	93	57	15	6
TiO_2/M1	0	97	53	30
TiO_2/M1	93	60	15	7
TiO_2/C1	0	58	35	21
TiO_2/C1	93	58	15	7

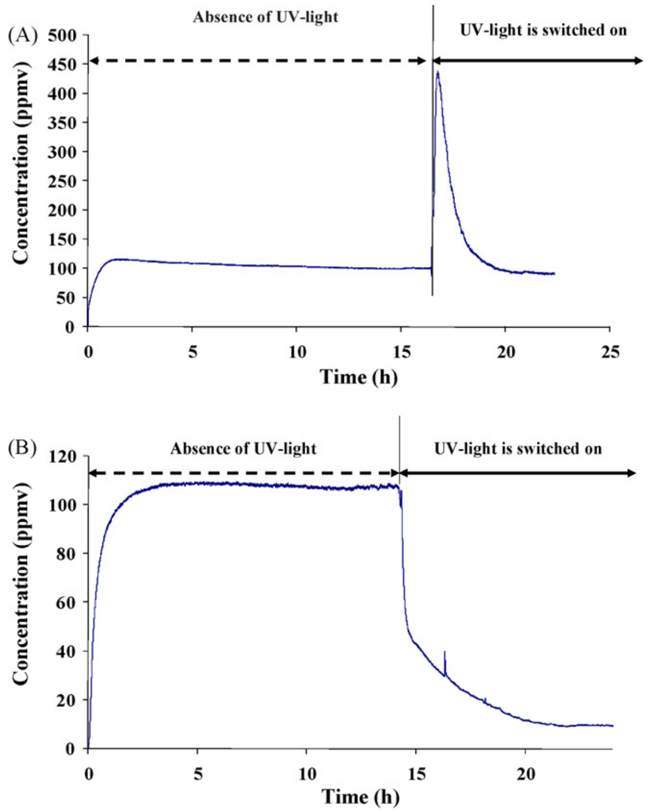

Fig. 5. Benzene photocatalytic oxidation by TiO_2/M1 in (A) absence of humidity and (B) presence of 93% R.H. (benzene flow rate 7.5 ml/min in both cases).

place, in agreement to previously published results [9–11]. The temperature of the bed during propene oxidation experiments in absence of humidity and using 30 ml/min of the propene stream was measured before the UV-light is switched-on and after (in stationary conditions). This temperature is 23 °C before the oxidation starts and gets to 38 °C in stationary conditions.

3.2.2. Benzene oxidation

In the present section, the oxidation of a low-concentration benzene stream (100 ppmv) is analysed in presence and absence of water vapour using the four mentioned catalysts. As stated in Section 1, some studies in the literature have been devoted to the oxidation of benzene at low concentration [2,7,8,12–32]. All these studies strongly differ in terms of their experimental conditions. Thus, benzene concentrations range from 35 ppb to 450 ppmv, the amount of P25 used varies from 0.15 to 1.64 g and the benzene-stream flow rates are usually in the range of 60–100 ml/min. The maximum benzene conversions depend on the humidity percentage, whose effect is still controversial, as stated in Section 1. Thus, typical benzene conversion percentages are in the range of 20–40% [17,24,25], and can get to percentages in the range of 60–90% in some experimental conditions [26].

As an example, Fig. 5A plots the oxidation of benzene (100 ppmv in air) in absence and presence of humidity for sample TiO_2/M1 at 7.5 ml/min flow rate. This figure shows that, in absence of water, there is a release of benzene when the UV-light is switched-on. Such benzene peak comes from the hydrocarbon that was adsorbed in M1 contained in the photocatalyst before UV-light is switched-on (experiments start after the photocatalyst is saturated with benzene). However, the most important information from this figure is that its catalytic activity is very poor and the stationary benzene concentration after the UV-light is switched-on is only slightly lower than the inlet benzene concentration. This means that the amount of benzene oxidised in such experimental conditions, in absence of humidity, is very low and only the release of adsorbed benzene takes place when the UV-light is switched-on.

In presence of water the photocatalytic oxidation of benzene is very different. Thus, as an example, Fig. 5B shows the effect of the presence of humidity. It can be seen that an important percentage of the hydrocarbon (90%) is oxidised when the UV-light is switched-on. Hence, the presence of humidity leads to an increase in the benzene conversion from 10% to 90%, keeping constant the rest of experimental conditions. This behaviour, opposite to that shown by propene, for which the introduction of water vapour in the stream to be oxidised is detrimental, is in agreement with previous results from the literature [17,23]. This is also the behaviour for the other three photocatalysts in presence of humidity.

Table 4 compiles the benzene conversion data in the different experiments carried out. The table shows that benzene conversion for TiO_2/M1 under such flow rate conditions and in absence of humidity is only 10%. This low activity seems to be related to the fact that the photocatalyst deactivates due to benzene cracking on its surface, which is in agreement with previously published data [16,17,21,22]. Thus, comparison between TiO_2/M1 pellets before and after being used for benzene oxidation in absence of humidity (see Fig. 6) clearly shows the pellets, initially white, becoming yellow-orange after this experiment, as a consequence of benzene cracking. A similar behaviour takes place for the oxidation of benzene using the other three photocatalysts in the different flow rates studied and in absence of humidity. Thus, Table 4 shows that the conversion at 7.5 ml/min is low for the other three photocatalysts: around 30% for P25, in powder form, 8% for P25-pellets and benzene oxidation does not take place when using TiO_2/C1. Benzene conversions are zero or close to zero for higher benzene-stream flow rates using the four photocatalysts in absence of humidity.

Table 4 shows that benzene conversion is 100%, 91% and 95% at 7.5 ml/min flow rate for samples P25, P25-pellets and TiO_2/C1,

Table 4
Benzene conversion using the four selected photocatalysts in presence or absence of humidity at different gas flow rates

Sample	Relative humidity (%)	Conversion at 7.5 ml/min	Conversion at 30 ml/min	Conversion at 60 ml/min
P25	0	31	5	3
P25	93	100	35	4
P25-pellets	0	8	0	0
P25-pellets	93	91	28	3
TiO_2/M1	0	10	0	0
TiO_2/M1	93	90	22	4
TiO_2/C1	0	0	0	0
TiO_2/C1	93	95	44	23

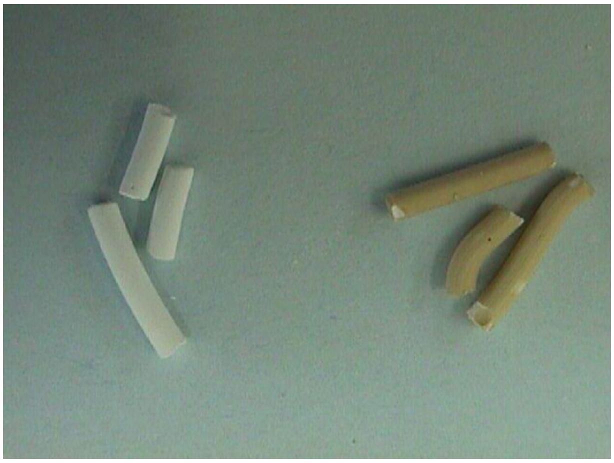

Fig. 6. TiO_2/M1 pellets before (left) and after their use for photocatalytic benzene oxidation (right) in absence of humidity.

respectively, in presence of 93% R.H. Thus, in all cases PCO is favoured in presence of water, independently of the flow and catalyst used. It is important to underline that the good performance of the photocatalysts in presence of humidity is linked to the fact that the oxidation of benzene in these conditions does not imply the formation of a yellow layer on the surface of the photocatalyst. Hence, under these conditions, benzene cracking is impeded.

To summarise these results, Fig. 7 plots, as an example, PCO of benzene at 30 ml/min flow rate. In absence of water vapour it can be seen that benzene conversion is very close to zero for the four photocatalysts used. Only for P25 there is some benzene conversion, but it is very small (5%). In contrast, in presence of 93% relative humidity all the photocatalysts showed an appreciable activity towards benzene oxidation. It is a remarkable fact that, in presence of humidity, the highest benzene conversion is achieved by sample TiO_2/C1, whereas in absence of humidity P25 was the best performing material.

As it was the case for propene, the effect of different relative humidity percentages on the photocatalytic oxidation of benzene has been analysed. Thus, Fig. 8 summarises these results for the oxidation of 30 ml/min benzene stream in absence of humidity and with different relative humidity percentages using P-25 pellets. This figure shows no oxidation activity in absence of humidity and that the introduction of humidity on the stream to be oxidised positively affects the achieved conversions, even for the lowest

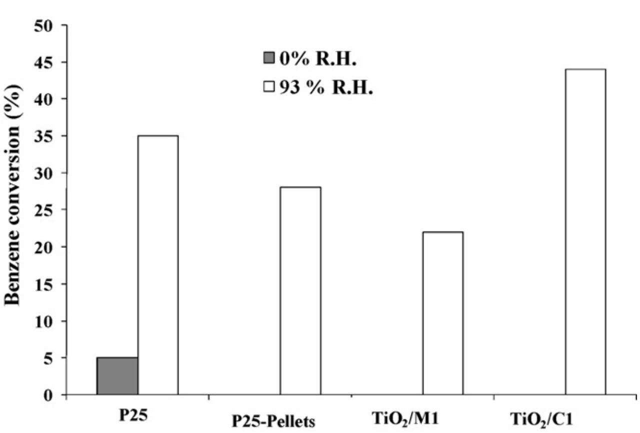

Fig. 7. Effect of the humidity on the oxidation of benzene by four different TiO_2-based photocatalysts (benzene flow rate 30 ml/min).

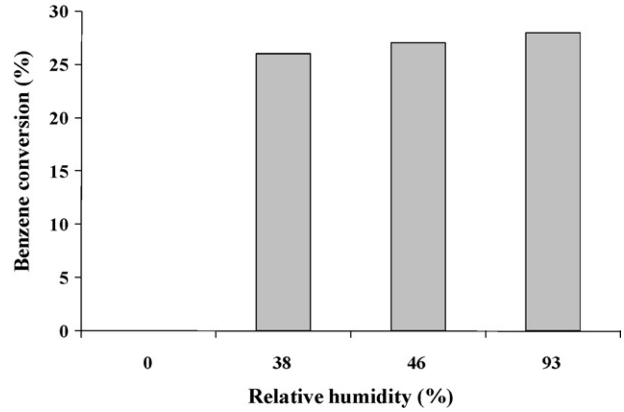

Fig. 8. Effect of different relative humidity percentages on the oxidation of benzene by P25-pellets (benzene-stream flow rate 30 ml/min).

relative humidity percentage studied. The activity remains essentially constant for the three relative humidity percentages, being very high even for relative humidity percentages close to 100%.

Comparison between the results from the present paper and those previously published shows that in the present study, as in that of d'Hennezel et al. [17], the introduction of humidity in the benzene stream to be oxidised is very positive for the final conversion. Thus, in the study of d'Hennezel et al. [17] the best results are achieved for 34% relative humidity percentage. A similar conclusion is achieved by Doucet et al. [23] in stationary conditions, showing that for long times the best conversion results are those for 30% relative humidity percentage, the highest one among those studied by the authors. Our results, as well as those from d'Hennezel et al. [17] and Doucet et al. [23], are different from those of Wang et al. [2] for which benzene conversion progressively decreases from 10% relative humidity.

The oxidation products of benzene have also been followed. If total benzene mineralization occurs, this would lead to six CO_2 molecules per molecule of benzene oxidised. However, the amount of carbon dioxide generated is, in most cases, lower than 50% of the amount expected. For 38% relative humidity percentage the amount of CO_2 generated is in the range of 40% of the carbon dioxide expected (if all oxidised benzene would be mineralised to CO_2). For higher relative humidity percentages (46% and 93%), the CO_2 generated is in the range of 27–35% of the carbon dioxide expected. Complete benzene mineralization does not occur since for benzene, much more difficult to oxidise than propene, intermediate oxidation compounds such as 4-hydroxyl-3-methyl-2-butanone and 2-hexanol are detected after UV-light is switched-on.

The temperature of the bed during benzene oxidation experiments in presence of 93% relative humidity using 30 ml/min of the benzene stream was measured before the UV-light is switched-on and after (in stationary conditions). Such conditions were selected considering that, in presence of humidity, benzene conversion is much higher than in its absence. This temperature is 23 °C before the oxidation starts and gets to 39 °C when the oxidation takes place at stationary conditions. Such temperature increase is expected considering the enthalpy of combustion of benzene (−3300 kJ/mol) and slightly higher than that for propene (whose enthalpy of combustion is −2060 kJ/mol).

3.2.3. Comparison between propene and benzene oxidation

The two previous sections have shown that the introduction of humidity, either in the propene or in the benzene stream, leads to slower oxidation kinetics in both cases in comparison to those in

absence of humidity. However, and despite this similarity, propene and benzene conversions show opposite behaviours. The introduction of water in the propene stream leads to a lower conversion, whereas in the case of benzene the presence of humidity in the stream to be oxidised leads to much higher conversions than those achieved when no humidity is present.

Comparison between the most active photocatalysts for the oxidation of propene from Table 3 (or Fig. 3) shows that in absence of humidity, the activity of the photocatalysts can be organised in decreasing activity order: P25 > TiO_2/M1 > TiO_2/C1 > P25-pellets. In presence of water, the photocatalysts activity relative order for propene oxidation does not apparently change: P25 > TiO_2/M1 ~ TiO_2/C1 ~ P25-pellets, although the achieved propene conversions are lower. The activity of the agglomerated materials can be explained considering the porosity of the additives and their affinity towards the adsorption of propene and water. The introduction of porous materials (M1 or C1) in the composition of the agglomerated photocatalysts leads to higher surface materials and hence, as expected, more active. The fact that the photocatalyst containing M1 is slightly more active than that containing C1 might be due to the fact that propene is more favourably adsorbed on MCM-41, according to previous published results which showed that propene adsorption in an inorganic-based catalyst, containing ZSM-5, was more favourable than in an activated-carbon-based one [44]. The lower propene conversion after the introduction of water could be related to the competitive adsorption of water in the adsorption sites, as it has been shown in previous studies for other hydrocarbons [45–47]. The water inhibitory effect has been observed, as an example, for isopropanol, acetone and trichloroethylene [48].

In the case of benzene, in absence of humidity, the decreasing activity order is P25 > TiO_2/M1 > P25-pellets > TiO_2/C1. However, the relative activity of the samples for the oxidation of benzene in presence of humidity is different: TiO_2/C1 > P25 > P25-pellets > TiO_2/M1. We must call the attention to the fact that sample showing poorer activity in absence of humidity, TiO_2/C1, is the most active one in presence of humidity. A possible explanation of the performance of the different photocatalysts for benzene oxidation could be related not only with adsorption, as it was the case of propene, but also with benzene cracking. In absence of water, benzene cracking, much more than benzene oxidation, is the reaction taking place, as shown in the previous section (see, Fig. 6). In such conditions, the presence of activated carbon seems to favour benzene cracking. In presence of water, benzene cracking seems to be limited, benzene oxidation being the main reaction taking place and hence, the most active photocatalyst is that containing C1, an activated carbon with a very high surface area and very high adsorption capacity towards benzene [49].

Finally, an explanation which could justify the different behaviour of benzene and propene in presence of humidity seems to be related to the adsorption equilibrium of both hydrocarbons in presence of water. Benzene adsorption on the activated carbon is preferred to water adsorption, according to the non-polar character of adsorbent and adsorbate and their adsorption parameters [50]. In the case of propene, whose adsorption is much less favourable than benzene adsorption [50,51], water adsorption competition is more important and propene displacement can take place.

4. Conclusions

The present paper focuses on the photocatalytic oxidation of two volatile organic compounds, benzene and propene, at low concentration (100 ppmv) using photocatalysts in powder form and agglomerated as pellets (containing or not additives). Comparison between the conversions in absence and presence of water is performed.

The results for propene show, despite the good conversions achieved in absence of humidity, that the introduction of humidity causes a decrease in conversion, and leads to slower propene oxidation kinetics. Such decrease in conversion is larger for increasing relative humidity percentages.

Active photocatalysts for benzene oxidation have been prepared in the form of pellets, showing that the composite pellet that contains activated carbon (70% TiO_2 and 30% activated carbon) possesses higher activity than the well-known P25 TiO_2 powder from Degussa.

The photocatalytic oxidation of benzene in water vapour-free streams is non-effective for any of the photocatalysts, showing a small benzene conversion (lower than 10% in the case of P25). Such low activity is related to benzene cracking.

The oxidation of benzene is noticeably favoured in the presence of water vapour and benzene conversion remains essentially constant for the three relative humidity percentages studied, 38%, 46% and 93%.

The relative activities of the four photocatalysts studied are different in presence or in absence of humidity for benzene photocatalytic oxidation. In absence of humidity, the best performing sample is P25, in powder, whereas in presence of humidity the agglomerated photocatalyst TiO_2/C1 is the most active.

Acknowledgements

The authors thank MCYT (CTQ2005-01358/PPQ) and Generalitat Valenciana (ARVIV 2007/063) for financial support.

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